

The Weird World of Nanoscale Gold

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Protagonists in the emerging field of nanotechnology have as their objective the design, construction and study of useful devices based on nanoscale materials and objects. Objects or structures that have at least one important dimension in the range 0.5 to perhaps 50 nm may be considered to be in the nanoscale domain. These sizes lie far below the 200 nm or so that can be resolved with an optical microscope, and are closer in size to the 0.3 nm diameter of individual atoms. The field of nanotechnology is attracting keen interest at present. The excitement is motivated by the observation that control of matter at the nanoscale holds the promise of, amongst others, faster computing, better medicines, and more useful materials. In this paper, the physical phenomena on which this optimism is based are broadly discussed and explained. Where appropriate, examples of the rather different and curious properties of gold at the nanoscale are used to illustrate the points covered.

Introduction

The existence of atoms was proposed by Democritus in 430 BC but their properties and behaviour were largely ignored until the pioneering studies of John Dalton circa 1800. Since then, the behaviour of individual atoms and molecules, and of macroscopic aggregates of them, has been the subject of intense study. However, one topic that was neglected until about 1990 was the synthesis and properties of nanoscale, non-molecular structures constructed from several dozens of atoms. This was despite the now famously prescient speculations of Richard Feynman on nanoscale devices in 1959 (1), in which the famous physicist predicted that the exploitation of matter in this way would provide unprecedented technological breakthroughs. Perhaps the reason for this omission was that the common tools of chemistry, such as the analytical balance, spectroscopy and X-ray diffraction, were not particularly useful when attempting to study structures with characteristic dimensions of the order of a few nanometers to a hundred nanometers. It is only recently that microscopy has routinely provided the means to characterize such objects. A particularly significant ‘enabling technology’ has been the scanning probe microscope, the first example of which was only invented in 1981 by the Nobel prize winners Gerd Binnig and Heinrich Rohrer (2). This new technology not only provided the ability to image the individual atoms or molecules on a surface, it also provided a means to manipulate them. This was demonstrated by early feats such as spelling out the letters ‘I B M’ by arranging individual atoms on a surface. Interest in exploiting the nanoscale and in nanotechnology has grown enormously since then, as even a casual search over the Internet will reveal. The purpose of this paper is to introduce the field to non-specialists, and in particular to explain what makes gold different and interesting at the nanoscale.

Some pertinent questions

What is nanotechnology?

A nanometer is one billionth, or 1×10^{-9} , of a metre. About four gold atoms, lined up side by side, make up a nanometer. Objects or structures that have at least one important dimension in the range 0.5 to perhaps 50 nm may be considered to be influenced by nanoscale phenomena. These sizes lie far below the 200 nm or so that can be resolved with an optical microscope, and were therefore not visible to us until the invention of electron microscopy in the twentieth century. Nanotechnology may be defined as the act of manipulating matter in this size range, most typically by producing useful, artificial, structures by assembling molecules or individual atoms into nanoscale artefacts. These new, artificial structures are not simple molecules or crystalline

phases, a point which differentiates nanotechnology from chemistry. In general, like most machines and complex devices, they are thermodynamically unstable.

How small is the nanoscale? I will try to put it into perspective. A typical full stop at the end of a sentence is about 300 μm in diameter. This is already pretty small. A little machine the size of a full stop would be amazing. But this is not nanotechnology. Even a bacterium cell is a hundred times smaller than a full stop. We need to go one thousand times smaller, so small that the nano-thing is to a single bacterium cell as the full stop is to us. That is the nano-scale.

Why the excitement?

Matter behaves rather differently at the nanoscale. For example, interatomic interactions and factors that are quite unimportant at macro-scales become dominant and, as will be shown shortly, many material parameters change markedly from those of the bulk material. Part of the excitement about nanotechnology is motivated by the observation that control of matter at the nanoscale is the key to faster computing, better medicines, and materials with in-built functionalisation (so-called 'smart materials'). This optimism is based not only on a consideration of the tremendous miniaturization that can be implemented at this scale (the point which Richard Feynman emphasized in his famous talk in 1959) but also on the benefits to be gained from exploiting the rather different physical and chemical properties of nanoscale structures. However, another reason for the great interest in nanotechnology is that it is very interdisciplinary, with a reach that encompasses chemistry, physics, biology, electronics and materials science. Current thinking amongst many makers of science policy is that such interdisciplinary activity is more likely to yield useful innovations than traditional discipline-based research.

There is unfortunately a lot of hype around nano-devices and nanotechnology, much of it initially stimulated by some futuristic technological predictions in popular literature (e.g. Drexler (3)). However, there is also considerable optimism, based on quite sober considerations, many of which we will discuss later. The areas in which the application of nanotechnology has led, or will shortly lead, to socially significant breakthroughs include medicine, solar energy, pollution abatement, computing, materials of construction, textiles and domestic hygiene. The US, Japanese and EU governments have earmarked billions of dollars for nanotechnology research; this commitment is matched by an expectation of meaningful returns!

Scissors, paper and rock

It was mentioned that nanotechnology involves assembling individual atoms or molecules into artificial, nanoscale, structures. Unfortunately, many of the possible structures are

(or would be, if we could make them) very chemically reactive, particularly in respect to oxidation. For example, in the case of metallic elements, the thickness of most passivating oxide layers is of the order of at least several micrometers. A nanoscale component made of such metals would be rapidly and completely consumed by oxidation, unless somehow protected. Of course, this is not a problem at all when stable *oxide* or *silicate* nano-particles or films are used (since they are already fully reacted with oxygen). This partially explains the rapidly growing popularity of diverse nanoscale oxides and silicates in applications as diverse as sun-screening cosmetics, polishing media for the silicon wafer industry, fillers in polymers, and self-cleaning/self-sterilizing coatings for architecture and the home.

However, many of the more interesting nanotechnological applications require a functionality beyond that which is readily imparted by oxides and silicates. In particular, there may be a need to conduct electricity, or to attach various complex organic molecules to the surface of the nano-structure. One solution is to try to protect the surface of the nanoscale electrical conductor or substrate from oxidation. Another, possibly better solution, is to select a material of construction that is free from this difficulty. The former strategy has been very successfully applied to components made of silicon, which can be passivated with a monomolecular film of an adsorbant such as hydrogen. This, and the enormous existing industrial infrastructure dedicated to silicon, explains why much of the current activity in nanotechnology involves silicon. Similarly, carbon nanotubes are resistant to oxidation because they too are passivated, in this case by the adsorption of one or more oxygen-containing species.

However gold and DNA are also frequently proposed for nanotechnological devices. Gold offers many of the 'top-down' fabrication advantages of silicon, and can be processed using electroless or electrolytic deposition, lithography and etching; all techniques familiar to the world's huge integrated circuit industry. It also has the advantage of being the least susceptible of all metals to oxidation. Furthermore, not only is gold a far better electron conductor than silicon, it also has a surface chemistry that is uniquely suited to attaching layers of sulphur-containing organic molecules, such as thiols and di-thiols, thereby additionally permitting 'bottom-up' assembly of quite interesting and promising structures. Regrettably, no simple way of making gold nano-wires has been found yet, but when one is, it may be expected that these would enter service in many of the applications for which carbon nanotubes are currently being punted.

DNA appears not to be an electrical conductor, despite some recent controversy on this point, e.g. Cingolani (4), but has a unique capability to be structured into complex 3-D

meso-structures by 'bottom-up' techniques. It also has the added feature that it is readily attached to gold and protein nano- and meso-structures, e.g. see Xiao (5). The possibility of multiple bio-technological applications for silicon/gold/DNA/protein nano-systems has inspired considerable research activity.

If silicon is the 'rock' of the nano-world, and DNA perhaps the 'paper' on which the information is written, then maybe gold will be the scissors, the tool that makes it all work together. This seems particularly true of gold nanoparticles, which are currently the subject of much interest by the scientific community, e.g. see Daniel and Astruc (6) who have very recently reviewed the properties and applications of these particles.

It is important to note that the relatively high value of gold is not expected to impede its penetration into these high-tech markets (7). The cost of the tiny amounts of gold used in existing or anticipated nanotech products is completely swamped by the overall added value of the product. Therefore, the manufacturers will use gold whenever it provides the best technological performance. A \$20 medical test kit or sensor might contain only gold worth 50 cents and yet it may be this critical ingredient that makes the whole device possible.

Some nanoscale weirdness

In the bulk form, gold is a soft, yellow metal, with the face centred cubic crystal structure, a melting point of 1064°C and excellent electrical conductivity. However, not one of these 'facts' necessarily applies at the nanoscale. Similar odd behaviour applies to most other elements and compounds. These new properties and phenomena are one of the things that the practitioners of this young field of nanotechnology seek to exploit.

Extraordinary surface area and chemical reactivity

The first, and perhaps most important point to note is that, at the nanoscale, there is a huge increase in the surface-to-volume ratio of any material. A significant proportion of any atoms in nanoscale structures are actually surface atoms. Therefore, the extent of any phenomenon or chemical reaction that occurs on the surface will be enormously amplified in nano-particulate or nano-porous materials. Figure 1 shows the increase in surface area possible merely by reducing the diameter of spherical particles of gold, while Figure 2 shows what can be achieved by decreasing the particle size of carbon. It is obvious that rather large values of specific surface area can be achieved, especially in carbon, due in this case to the latter's very low density relative to that of gold. The huge increase in surface area available from nanoscale materials is used to make heterogeneous catalysts, and specialized filters, to name only two applications.

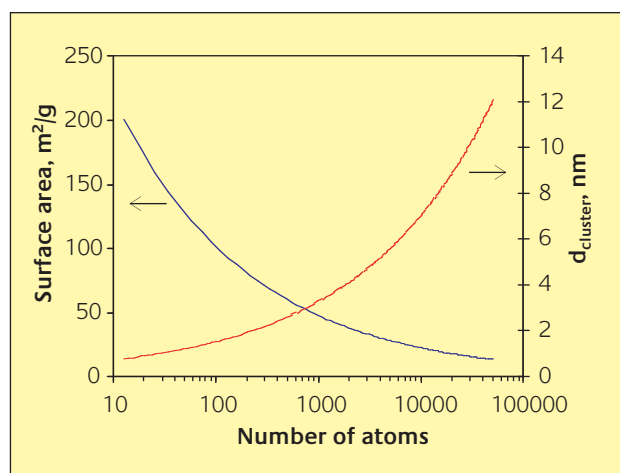


Figure 1

Approximate size and specific surface area of spherical nano-particles of gold

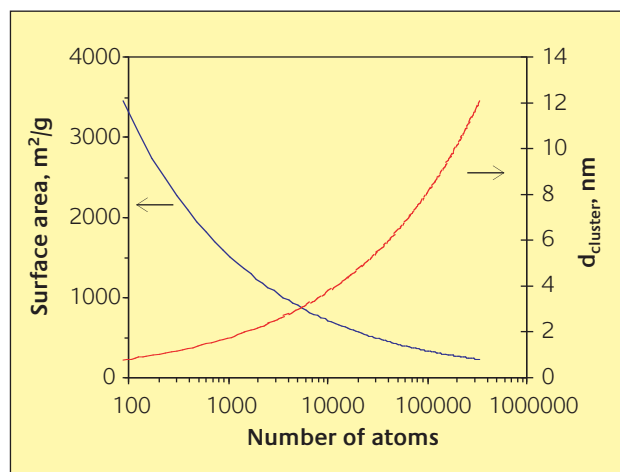


Figure 2

Approximate size and specific surface area of spherical nano-particles of carbon

Of course, in many practical situations the material is actually used as a nano-porous aggregate, rather than as little spheres, but the mathematical trends will be the same. Ordinary activated carbon can reach over 1000 m²/g, while the special form of graphite known as a nano-scrolls (8) can reach over 2000 m²/g. Gold of course, is a considerably heavier element than carbon, which is a huge handicap in terms of specific surface area. However, the figures of 2 m²/g for mesoporous gold cited in some literature (9) can be boosted to just over 20 m²/g by careful synthesis (10), and it is evident that in principle at least, a loose aggregate of gold nano-particles of, for example, 2 nm diameter could exhibit as much as 150 m²/g.

By the way, it is believed that the interesting heterogeneous catalytic ability of gold is intimately linked to its surface properties at the nano-scale, although it is not that

simple to discover whether this is simply an effect of increased specific surface area, or of changed electronic properties, or of an increase in the number of special active sites (11). But, whatever the explanation proves to be, nano-technology and heterogeneous catalysis by gold are inextricably linked.

Strange colours

Bulk gold has a familiar yellow colour, caused by a reduction in reflectivity for light at the blue end of the spectrum (12). However, if we sub-divide the gold into smaller and smaller particles, there comes a point at which the particle size becomes smaller than the wavelength of the incident radiation. New modes of interaction of the light with the gold become prominent, in particular interactions involving electronic oscillations called surface plasmons. When the particles of gold are small enough their colour is ruby red, due to their strong absorption of green light at about 520 nm, corresponding to the frequency at which a plasmon resonance occurs with the gold. This effect has been used to colour glass, even in Roman times. However, if such tiny particles are allowed to coalesce in a controlled fashion, their colour can be systematically varied from pink through violet to blue (13), as in Figure 3. This is due to a change in their absorption spectrum on aggregation, caused by increasing absorbance of the red wavelength of light. This phenomenon has been invoked as a colorimetric indicator in home pregnancy tests (14) and for testing for specific genetic sequences (15). Also, interesting non-linear optical effects are possible using gold nano-particles (16), which may find application some day in opto-electronic circuitry.

Actually, many other metals display this type of spectrally-selective resonance too, but in general the resonant frequency lies out of the visible range, in the near ultra-violet. Furthermore, gold is one of the very few metals noble enough to survive as a nano-particle under atmospheric conditions. This serendipitous combination of properties has

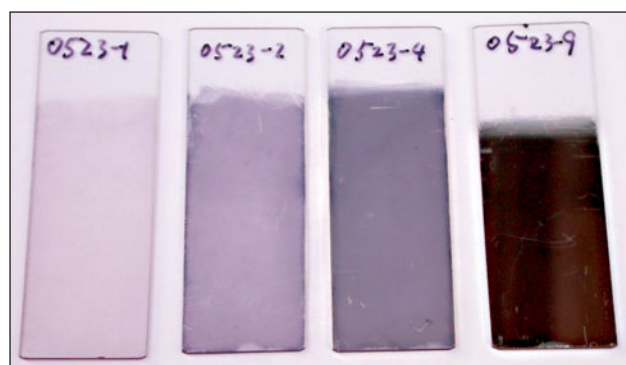


Figure 3

Glass slides that have been coated to varying extents with gold nano-particles, photo courtesy of Mr X. Xu, University of Technology Sydney

encouraged its application in a diverse range of niche applications.

Recently, another strange optical effect at the nanoscale has been highlighted. Layered metallic nano-particles, such as nano-shells which consist of gold deposited onto a tiny dielectric core, have completely different optical properties to ordinary nano-particles. These structures absorb in the near infra-red rather than in the visible (17), and are under development for possible medical applications, such as in tumour destruction. Similar unusual optical tuning may be achieved with gold nano-rods of varying aspect ratios (18).

Unusual crystal structures

Bulk gold is face centred cubic (fcc), and the occasional rare crystals of native gold exhibit the highly symmetrical cubic, octahedral or rhombododecahedral crystal forms associated with the fcc structure (19). This generalization remains true down to particles of about 10 nm in size (which contain about 28,000 atoms of gold) but for even smaller sizes the situation is more complex. There is considerable debate regarding the structure and external form of nano-particles of between 1 and 10 nm (20). This debate has been exacerbated by the difficulties inherent in trying to physically characterize such tiny objects. As a result, several attempts have also been made to predict the structure of gold nano-particles by calculation. In general, the results of these calculations are not in complete agreement, either with each other or with the results of experimental techniques. Conflicting claims are made for icosahedral or decahedral

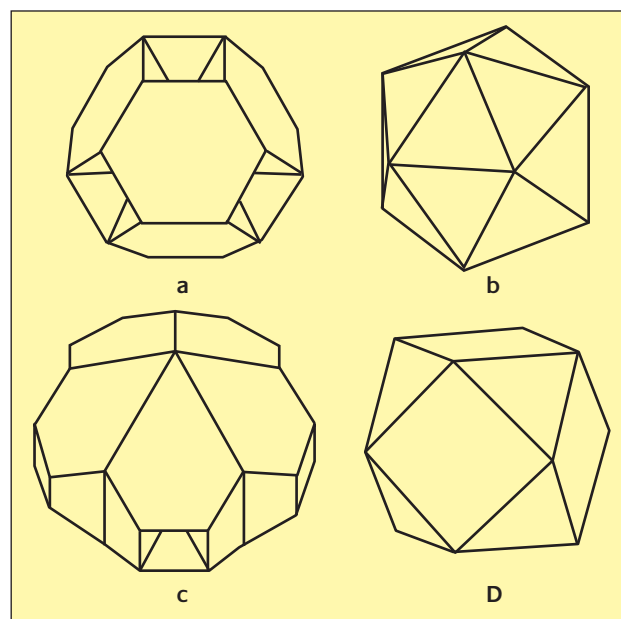


Figure 4

Some shapes of gold nano-particles, (a) truncated octahedron, (b) icosahedron, (c) Marks decahedron and (d) cuboctahedron (from Cortie and van der Linde (10))

quasi-crystal structures, amorphous structures, or octahedra, cuboctahedra and truncated octahedra based on the fcc structure (Figure 4). The icosahedral and decahedral structures have five-fold symmetry and are non-crystalline in the sense that they cannot be packed together to make macroscopic crystals. They are structures that exist only in the nanoscale domain.

Why does the structure of gold change at the nanoscale? The crystal structure of the elements in the bulk state is largely determined by their electronic configurations, and the element will adopt the packing arrangement that minimizes its free energy. However, as we have seen, for nano-particles the surface atoms become a hugely significant factor. Now the internal energy of the substance must be minimized with respect to electronic configuration and surface energy and elastic strain. It appears that the icosahedron yields an efficient compromise between surface area and packing density (21), whereas certain decahedra (an example of which is the Marks decahedron) which have re-entrant facets, are said to offer a compromise between surface area and strain energy (20).

Studies of gold nano-particles have apparently found all the above structures, with their presence seemingly depending very much on the particular experimental conditions. However it has been said that icosahedra and Marks decahedra will tend to dominate any actual experimental particle dispersion in the sub-5 nm range (20,22). This is the size range to which the catalytic activity of gold is normally attributed. To put this in context, a hemisphere of 5 nm diameter would contain about 2,600 gold atoms, whereas one of 3 nm diameter would contain only about 500 atoms. A Kruggerand coin of one troy ounce however contains about 95,090,000,000,000,000,000,000 atoms of gold, a number so big as to be beyond human conception.

Anomalous melting points

Bulk gold melts at 1064°C. However, not even this property is constant as the scale of the structure is shrunk into the nanoscale. The melting point of gold nano-particles is depressed from that of the bulk material. The reason for this phenomenon is, once again, the huge increase in surface area of gold nano-particles.

The results of two studies for particles are shown in Figure 5, drawn from the calculations of Liu *et al.* (23) and measurements of Dick *et al.* (24). The data differ considerably, but even taken conservatively, these calculations indicate that catalytically active gold particles in the 5 nm size range ($\sim\text{Au}_{3600}$) would be molten at about 830°C, particles of about 2 nm (about Au_{200}) would liquefy at 350°C and, by extrapolation, particles of about 1 nm ($\sim\text{Au}_{30}$) diameter would be molten at 200°C!

This effect is not peculiar to gold of course, and direct observation of it under a microscope has been made in the case of the element indium, the bulk state of which melts at

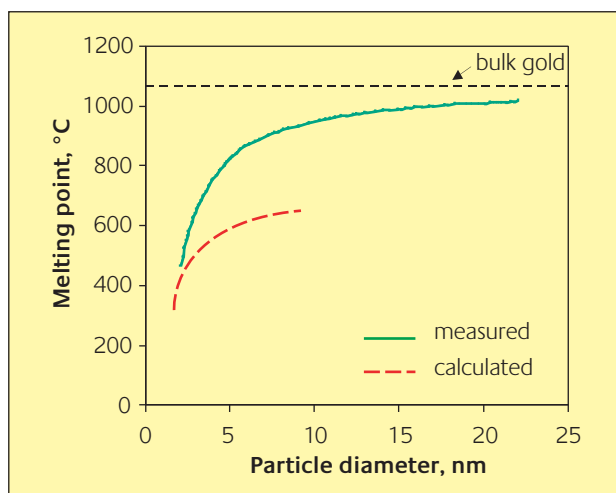


Figure 5

Melting point of gold nano-particles as a function of particle diameter

152°C. The melting point of 8 nm diameter nano-particles of indium has been directly observed to be only 25°C (25). The melting point of even smaller particles of this element may lie below 0°C, a truly strange state of affairs.

Curious magnetic properties of some elements

Another property that can produce surprises at the nanoscale is magnetism. Aluminium metal, for example, is not at all magnetic in the bulk form. However, tiny clusters of 13 aluminium atoms, which measure of the order of 0.8 nm across, are actually magnetic (26). The reason is complex, and has to do with their electronic configuration. No similar phenomenon is known yet for gold, however the issue of

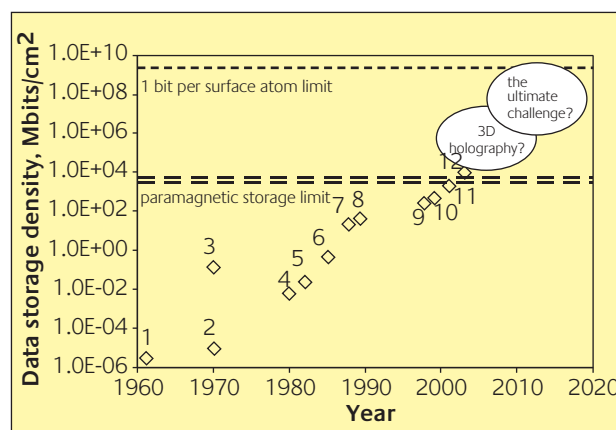


Figure 6

Development of data storage density as technology starts to exploit the nanoscale domain (redrawn from Eberhard (26) with addition of new data by present author). Milestones: 1. punch card, 2. core memory, 3. first inductive read head, 4. Apple II floppy disk, 5. DEC 1.2 MB floppy disk, 6. 157 MB hard disk, 7. compact disk (CD), 8. 415 MB hard disk, 9. IBM 340 MB Microdrive, 10. DeskStar hard disk, 11. IBM 1 GB Microdrive, 12. first IBM 'pixie dust' media

nanoscale magnetic properties is raised here because of the significant role that they have played in computer technology. In particular, this has provided a growing niche market for some of the platinum group metals. The magnitude of bulk magnetic properties changes as the dimensions of the materials approach the nanoscale, and the magnetic moment per atom rises sharply (26). FePt nanoparticles in the 30 to 100 nm size range, which have extremely high coercivity, are already in widespread use for coating the hard disks of computers for this reason. Even greater densities of data storage seem possible if only the particle size could be reliably made smaller, however both oxidation and the so-called paramagnetic storage limit are problems. Yet, a major breakthrough in this field occurred in 2001 when IBM researchers announced that the introduction of a layer of ruthenium only three atoms thick (which they called 'pixie dust') enabled them to quadruple data storage densities (Figure 6), thereby simultaneously breaking the paramagnetic limit and demonstrating what surprises lie in store for researchers of the nano-domain. Once again, the cost per gram of the element used is not particularly important when such small amounts are consumed per device.

Tunnelling electrons, quantized charge and white LEDs

Some of the most interesting ideas for exploiting the nanoscale domain arise from the odd electronic phenomena that occur at this scale. It is well known that electric current in most (but not all) conductors is associated with the movement of electrons, and that this can occur in metallic conductors or in semi-conductors. However, these 'classical' observations are not entirely accurate at the nanoscale. In the first manifestation of this weirdness, consider the case of a single, gold nano-particle, placed between two wires in an electric circuit but separated from them by a tiny gap, of say, 1 nm on each side (Figure 7). Classically, no current would flow through this arrangement. But at the nanoscale, the physical dimensions of the objects have begun to approach those of quantum quantities such as the density distribution function of electrons. These distributions do not terminate sharply at the supposed surfaces of the objects but, rather, tail off gradually. The net result is that if you position two conductors so that they are close together but not actually touching, and apply a voltage between them, then there is a probability that electrons will actually 'tunnel' through the gap between them. An electric current will flow even though there is no physical contact. So the circuit in Figure 7 can conduct current, a feature which has led to it being proposed as the basis of a single electron transistor or SET whose current flow is modulated by a bias on the third, gate electrode (27). However, consider what happens when a single electron has been induced to tunnel from electrode A

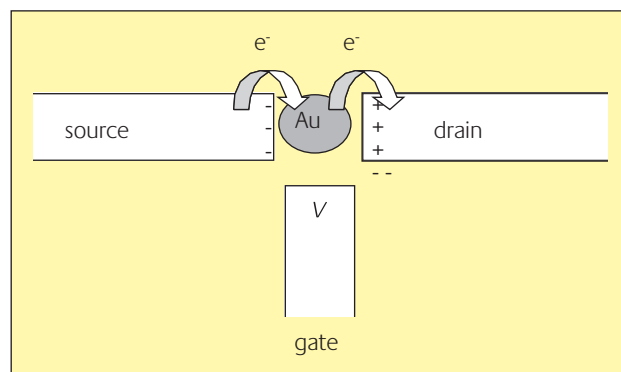


Figure 7

Single electron transistor based on a gold nano-particle, showing how voltage V on gate electrode controls tunneling of electrons into and off gold nano-particle inserted between source and drain electrodes

to the gold particle. Now there is a net negative charge on the gold particle (at least until this electron tunnels in turn to electrode B). The excess negative charge, while it lasts, will repel any subsequent electrons tunnelling events from A. Alternatively, no further current will flow until the voltage has been increased enough to overcome the repulsion of the electrons already on the nano-particle. So at the nanoscale, electric current may proceed in a kind of jerky way, in this case caused by the combination of what is known by a Coulomb blockade and of tunnelling. The overall result has been termed a Coulomb staircase (28). Nanoscale weirdness of this kind has been used to produce a variety of interesting new electronic devices, such as the resonant tunnelling diode. The exploitation of yet other nanoscale phenomena have led to the development of the latest generation of coloured LEDs, which offer conversion efficiencies that now rival those of incandescent lighting (29).

It is worth pointing out that gold is the leading candidate for all manner of nano-sized electrical conductors. This is due to its excellent conductivity and resistance to oxidation. A nanoscale wire of almost any other metal would spontaneously oxidize in air and would crumble to a pile of oxide dust. Therefore, most schemes for molecular electronic devices invoke a gold wire or two in their design. Recently, vapour-deposited gold has even been used as a brazing agent to weld two electrodes onto a carbon nanotube of 100 nm diameter (30).

Different electronic configurations

Bulk gold is a renowned conductor of electricity, with a conductivity that is beaten only by copper and silver. This property arises directly from its electronic configuration. However, even this familiar 'fact' is overturned at the nanoscale. Gold structures at the bottom end of the nanoscale may, depending on shape and substrate, actually be semi-conductors with a significant band gap [31]. The

transition occurs at a size dependent on the chemical environment, and will be somewhere between 1 and 3 nm (26,31), corresponding to a hemispherical cluster with between 15 and 150 atoms. The special electronic configuration of very small nano-particles results, in part, from the fact that their physical dimensions are smaller than the characteristic dimension of the electron wave function of the bulk material. Such tiny particles, termed quantum dots or artificial atoms if they are disc-shaped, have been proposed as the basis of a new generation of nano-scale electronic devices (27).

The catalytic activities of such exceedingly small clusters have been found to be acutely size dependent, peaking in one example at a cluster diameter of close to 3 nm, and falling sharply within 0.5 nm either side (31). One interpretation of this is that the best catalytic activity is actually derived from a particular value of the band gap, and too great a gap, or none at all, is less favourable. It should be noted that gold is not unique in this respect, and that other noble metals, such as Pd and Pt, exhibit similar properties (26,31).

Enhanced strength and toughness

The strength and toughness of both ceramics and metals can be enormously enhanced if they are made out of nanoscale crystallites rather than the usual micron-sized grains. This effect is already widely exploited to make superior ceramics and tungsten carbide-cobalt composites. Ceramics made from nanoscale TiO₂ particles not only sinter together 600°C lower than normal, but also possess enhanced strength and toughness (32). There is a similar effect in metal systems. Nano-crystalline copper, for example, is up to five times stronger than ordinary copper (Figure 8). In this case the explanation relies upon the observation that deformation in metals is generally carried by lattice defects called dislocations, and nanoscale copper crystals are actually too

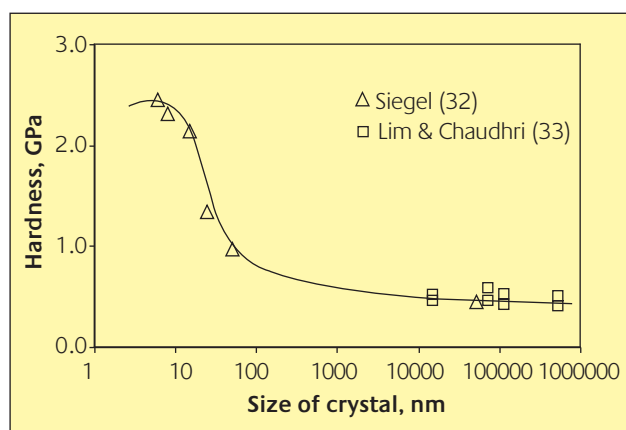


Figure 8

Hardness of copper as a function of its grain size (redrawn from data of Siegel (32) and Lim and Chaudhri (33)). Gold follows a similar trend

small to even contain dislocations (32), thereby hugely magnifying the strengthening already well-known to arise from reduced grain sizes. In a related manifestation of this effect, comparatively ductile metals such as aluminium may be strengthened by a process known as equiangular extrusion, which refines the grain size of the aluminium into the nanoscale, and which can be used to make what is otherwise quite a soft material into something springy and hard. Similar behaviour is exhibited in gold.

Conclusions

It has only been possible to skim through the subject of nanotechnology and the nanoscale in this overview. The emphasis has been on showing how and why materials and phenomena at this scale are different, and how this affects the properties of gold. Gold is one of the very few metallic elements that can be used in nanoscale devices and systems due to its resistance to oxidation. In addition, gold at the nanoscale has a variety of additional and unexpected properties not observed at the macroscale. For example, its colour changes from the bright yellow of the bulk phase to the reddish-purple of its nano-particles, its electrical conductivity decreases to the point where it becomes a semiconductor, its strength soars but its melting point falls to not far above room temperature and, finally, the crystal structure of gold nanoparticles is not even necessarily face centred cubic. The worldwide interest in nanotechnology is motivated by the fact that exploitation of the strange behaviour of nanoscale structures unlocks all kinds of exciting new commercial and scientific opportunities.

About the Author

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